

Citation for published version:

Lee, KP, Arnot, TC & Mattia, D 2011, 'A review of reverse osmosis membrane materials for desalination-development to date and future potential', *Journal of Membrane Science*, vol. 370, no. 1-2, pp. 1-22.
<https://doi.org/10.1016/j.memsci.2010.12.036>

DOI:

[10.1016/j.memsci.2010.12.036](https://doi.org/10.1016/j.memsci.2010.12.036)

Publication date:

2011

Document Version

Peer reviewed version

[Link to publication](#)

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Title

A Review of Reverse Osmosis Membrane Materials for Desalination – Development to date and Future Potential.

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Abstract

Reverse osmosis (RO) is currently the most important desalination technology and it is experiencing significant growth. The objective of this paper is to review the historical and current development of RO membrane materials which are the key determinant of separation performance and water productivity, and to define the targets for those who are developing new RO membrane materials. The chemistry, synthesis mechanism(s) and desalination performance of various RO membranes are discussed from the point of view of membrane materials science. The review starts with the first generation of asymmetric polymeric membranes and finishes with current proposals for nano-structured membrane materials. The review provides an overview of RO performance in relation to membrane materials and methods of synthesis.

To date polymeric membranes have dominated the RO desalination industry. From the late 1950s to the 1980s the research effort focussed on the search for optimum polymeric membrane materials. In subsequent decades the performance of RO membranes has been optimised via control of membrane formation reactions, and the use of poly-condensation catalysts and additives. The performance of the state-of-the-art RO membrane has been highlighted. Nevertheless, the advances in membrane permselectivity in the past decade has been relatively slow, and membrane fouling remains a severe problem.

The emergence of nano-technology in membrane materials science could offer an attractive alternative to polymeric materials. Hence nano-structured membranes are discussed in this review including zeolite membranes, thin film nano-composite membranes, carbon nano-tube membranes, and biomimetic membranes. It is proposed that these novel materials represent the most likely opportunities for enhanced RO desalination performance in the future, but that a number of challenges remain with regard to their practical implementation.

Keywords: Desalination, Reverse osmosis (RO), Membrane material, Membrane performance, Nano-materials.

Research Highlights

- ▶ State-of-the-art RO membrane system performance
- ▶ Material science development of conventional polymeric membrane
- ▶ Recent research breakthrough of novel nano-structured RO membrane

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1. Introduction

Today reverse osmosis (RO) is the most widely used desalination technology globally. Over the past few decades remarkable advances have been made in the preparation of RO membranes from different materials. Despite this, reviews of RO membrane materials have been rare, probably due to the fact that RO membranes of current practical importance are mainly based on patents rather than conventional research journal papers. The last published comprehensive review on RO membrane materials was by Petersen more than 17 years ago [1] and, naturally, only focused on the thin film composite membranes which existed at the time. Recently, Li and Wang published a review of research on surface modification of RO membranes [2]. In addition to ongoing research into conventional polymeric RO membrane materials, nanotechnology has opened the way to incorporating nanomaterials into RO processes. It therefore seems timely to comprehensively review the historical development of commercially successful RO membrane materials and to look forward to the novel nano-structured materials that will shape future trends in membrane materials research.

1.1 Current and Projected Needs of Clean Water Resources

The famous Malthusian doctrine states that ‘population increases in a geometric ratio, while the means of subsistence increase in an arithmetic ratio’ [3]. This is illustrated by the fact that global fresh water demand increases by a factor of six between 1900 and 1995, an increase of more than double compared to the concurrent increase in population [4]. Since 1995 this trend has further accelerated, due to simultaneous increases in water use in emerging economies and reduction in fresh water availability due to pollution and the effects of climate change. The lack of access to potable water and sanitation is a major source of disease and an obstacle to sustainable growth for a large part of the global population [5, 6]. Many developing countries are undergoing rapid industrialization without appropriate wastewater management systems, and are now facing increasing water pollution issues whilst still struggling with poor water supply and sanitation problems [7]. According to the World Health Organization, there are more than 2.5 billion people (about 40 % of the world’s population) that do not have access to sewer sanitation systems [8]. At the same time sustainable provision of clean water resources is important to all economies irrespective of their size. The shift to biofuels may add further significant demands for water for crop irrigation and product manufacturing and refining [9]. In many cases, natural water supplies

are decreasing as a result of climate change and over exploitation, and solutions such as water conservation and water transport, or construction of new dams, are insufficient to cope with increasing demand. Therefore the most pressing challenges today include the recovery of clean drinking water from salty or sea water, by far the most abundant global water resource, and the treatment and recycle of wastewater.

Desalination, a technology that converts saline water into clean water, offers one of the most important solutions to these problems [10]. As shown in Figure 1, the amount of contracted capacity in desalination plants grew by 43 % in 2007, to 6.8 million m³ per day, up from 4.7 million m³ per day in 2006. In the first half of 2008 growth in contracted capacity was 39 %, and the total global desalination capacity was about 50 million m³ in 2009 [11-13].

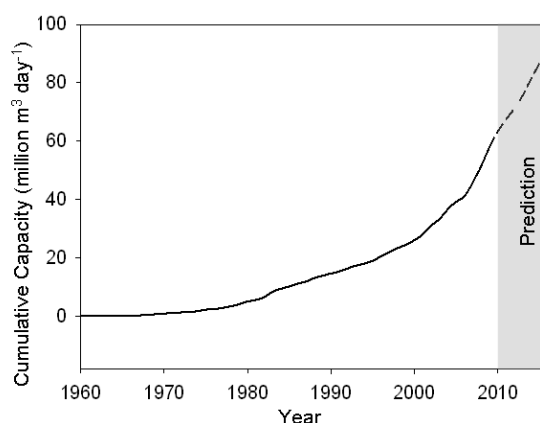
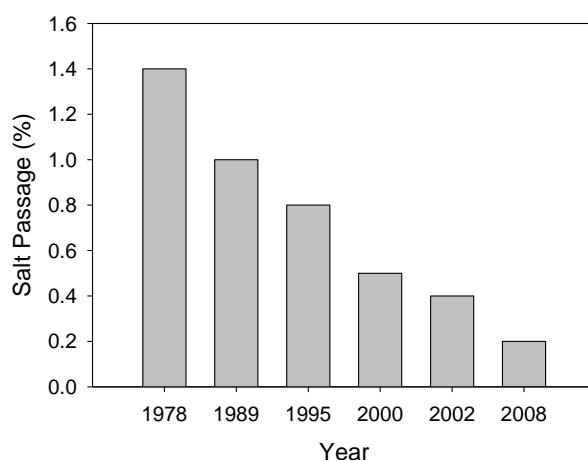


Figure 1. Cumulative desalination capacity from 1960 to 2016 [12, 13].

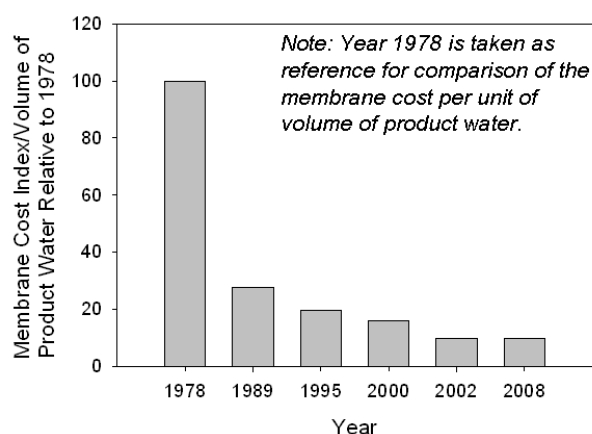
1.2 Current State-of-the-Art RO Technology

RO is today the leading desalination technology. It has overtaken conventional thermal technology such as multi-stage flash (MSF) [14] and is expected to maintain its leadership in the near future though new technologies such as membrane distillation [15], electrodialysis [16], capacitive deionization [17] and forward osmosis [18] that have been proposed. Commercial interest in RO technology is increasing globally due to continuous process improvements, which in turn lead to significant cost reductions. These advances include developments in membrane materials and module design, process design, feed pre-treatment, and energy recovery, or reduction in energy consumption. The beneficial outcomes are shown quantitatively in Figures 2(a), (b) and (c). The seven-fold increase in salt rejection performance over 30 years has greatly expanded the range of saline feeds that can be treated

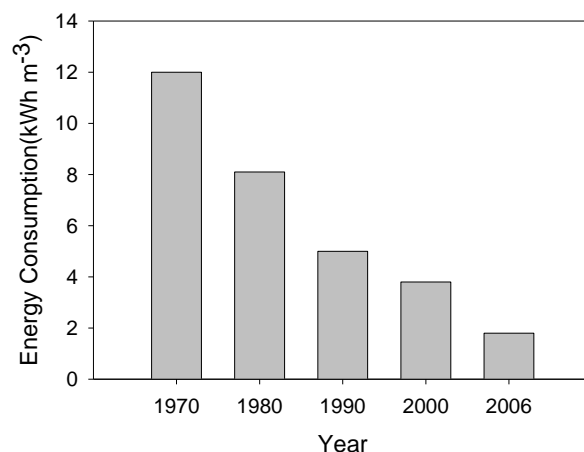
to meet the stringent potable water standards. The enhanced mechanical, biological and chemical strength of RO membranes, as well as increased permeability, have reduced the membrane cost per unit volume of water produced by more than 10 times since 1978. The combined effort to minimise fouling and concentration polarization, in addition to maximise permeate flux and energy recovery, has decreased the energy consumption from 12 kWh m^{-3} in the 1970s to less than 2 kWh m^{-3} in 2006 [19, 20].



(a)



(b)



(c)

Figure 2. (a) Improvement in salt rejection. *Data from [19];*

(b) Reduction in membrane cost. *Data from [19];*

(c) Reduction in energy consumption of RO. *Data from [20]*

Nevertheless, the greatest efficiency gains have arisen from the improvement of the membranes. The structure, material, and morphology of RO membranes have been modified to improve functionality (permeability and selectivity) and applicability (mechanical, chemical and biological stability). The current RO membrane market is dominated by thin film composite (TFC) polyamide membranes consisting of three layers : A polyester web acting as structural support (120 – 150 μm thick), a micro-porous interlayer (about 40 μm) and an ultra-thin barrier layer on the upper surface (0.2 μm) [21]. The polyester support web cannot provide direct support for the barrier layer because it is too irregular and porous. Therefore, between the barrier layer and support layer, a micro-porous interlayer of polysulfonic polymer is added to enable the ultra-thin barrier layer to withstand high pressure compression. The thickness of the barrier layer is reduced to minimize resistance to permeate transport. Membrane pore size is normally less than 0.6 nm to achieve salt rejection consistently higher than 99 %. The selective barrier layer is most often made of aromatic polyamide, for example via interfacial polymerization of 1,3 phenylenediamine (also known as 1,3-benzenediamine) and the tri-acid chloride of benzene (trimesoyl chloride) [22]. With improved chemical resistance and structural robustness, it offers reasonable tolerance to impurities, enhanced durability and easy cleaning characteristics [1, 23, 24].

The spiral wound membrane module configuration is the most extensively used design in RO desalination. This configuration offers high specific membrane surface area, easy scale up operation, inter-changeability, low replacement costs and, most importantly, it is the least expensive module configuration to produce from flat sheet TFC membrane [25, 26].

Although the spiral wound configuration was developed decades ago, improvements in the dimensions of spacers, feed channels and vessels, as well as the materials of construction, have optimised the inter-connection between module design and fluidic transport characteristics, thereby decreasing both fouling and pressure losses.

Polyamide spiral wound membranes dominate RO / Nanofiltration (NF) market sales with a 91 % share. Asymmetric cellulose acetate (CA) hollow fibre membranes hold a distant second spot [27]. Although the latter has superior chlorine resistance, thereby allowing prevention of the growth of microorganisms and algae via chlorine injection, the former has higher salt rejection and net pressure driving force [28]. There are four major membrane module suppliers which provide RO membranes for large scale desalination plants, namely DOW, Toray, Hydranautics and Toyobo. Hence, state-of-the-art seawater desalination RO membrane modules from each supplier are tabulated in Table 1 in order to provide a benchmark of current SWRO performance. A specific comparison of the various products is not attempted as the data corresponds to different test or operating conditions [29-36].

Research on the design of modular elements is currently focusing on optimization of hydrodynamics in order to minimise the concentration polarization effect. In addition, larger modular elements are desirable for increased desalination capacity. Recently, Koch Membrane Systems have released 18-inch spiral wound modules with the MegaMagnum[®] trade name. Hydranautics and DOW FILMTEC[™] have 16-inch modules which are being piloted in cooperation with the national water agency in Singapore, PUB. Studies have shown that such module design can further decrease the cost of desalination by approximately 20 % [37, 38].

Table 1. Some of the state-of-the-art SWRO membrane modules in application

Membrane module brand name	Material & module	Permeate flux ($\text{m}^3 \text{ day}^{-1}$)	Salt rejection (%)	Specific energy consumption ^[d] (kWh m^{-3})
DOW FILMTEC™ 8 inch SW30HRLE	TFC crosslinked fully aromatic polyamide spiral wound	28.0 ^[a]	99.60 – 99.75 ^[a]	3.40 (2.32) ^[e] at Perth SWRO Plant, Australia [30]
Hydranautics 8 inch SWC4+	TFC crosslinked fully aromatic polyamide spiral wound	24.6 ^[b]	99.70 – 99.80 ^[b]	4.17 (2.88) ^[e] at Llobregat SWRO Plant, Spain [30, 33]
Toray 8 inch TM820C	TFC crosslinked fully aromatic polyamide spiral wound	19.7 – 24.6 ^[a]	99.50 – 99.75 ^[a]	4.35 at Tuas SWRO Plant, Singapore [31]
Toyobo 16 inch HB10255	Asymmetric cellulose tri-acetate hollow fibre	60.0 – 67.0 ^[c]	99.40 – 99.60 ^[c]	5.00 at Fukuoka SWRO Plant, Japan [32]

Note: [a] Test condition: 32 g L⁻¹ NaCl solution, 55 bar, 25 °C, pH 8 and 8 % recovery [29, 35];

[b] Test condition: 32 g L⁻¹ NaCl solution, 55 bar, 25 °C, pH 7 and 10 % recovery [34];

[c] Test condition: 35 g L⁻¹ NaCl solution, 54 bar, 25 °C and 30 % recovery [36];

[d] These numbers should not be compared explicitly because of different operating parameters (*e.g.* feed water quality, recovery, pre-treatment processes, process design, etc.) at different desalination plants.

[e] The number in brackets is the energy consumption for the RO unit.

1.3 Challenges and Trends in RO Desalination Technology Development

Sheikholeslami recently concluded that the future challenges in the desalination industry include feed water characterization, process development, materials development, renewable energy source, stringent water standard and brine management [39].

Currently the largest SWRO plant in the world is in Ashkelon, Israel, and it has a production rate of about 110 million m³ year⁻¹. Considering the global average water consumption per capita of 1,243 m³ year⁻¹ (5 % for domestic use, 85 % for agricultural irrigation, and 10 % for industrial use) [40], this plant can supply fresh water to less than 100,000 people. Hence mega-sized desalination plants must be developed if we are to provide new clean water supplies to billions of people.

In this context, the biggest challenge would be making RO desalination affordable for poorer countries. Unarguably, the capital investment and operating costs of RO plants must be further reduced to achieve this. Electricity (energy), labour and chemicals make up about 87 % of the total RO cost [14]. Developments in membrane material and module optimization can significantly contribute to the reduction of all three aspects.

Additionally, significant improvement in the rejection of low molecular weight compounds, especially boron species, is necessary. The highest boron rejection membrane offered in the market can only achieve 93% boron rejection at optimum conditions, and it has been reported that 99% of boron rejection is required in the Middle East region for one-pass RO process to comply with the WHO's water drinking standard [41]. Furthermore, higher salt rejection can possibly reduce the number of RO passes necessary to achieve appropriate product water quality. Reduction in fouling, particularly via the development of chlorine-tolerant membranes, is important because it directly reduces the costs of membrane replacement, backwashing chemicals, and energy to overcome the additional osmotic pressure.

Although the operating pressure in current systems is already close to the thermodynamic limit and a further reduction would have a modest impact on performance [42], the reduction in energy consumption would be considerable, as the energy cost represents half of the total water production cost. Moreover higher permeability would lead to a reduction in membrane area, and consequently a reduction in membrane replacement costs, a smaller plant foot print and a reduced use of cleaning chemicals. To be of commercial interest, any novel membrane must outperform the materials and modules listed in Table 1.

2. Conventional Desalination RO Membranes – Polymeric Materials

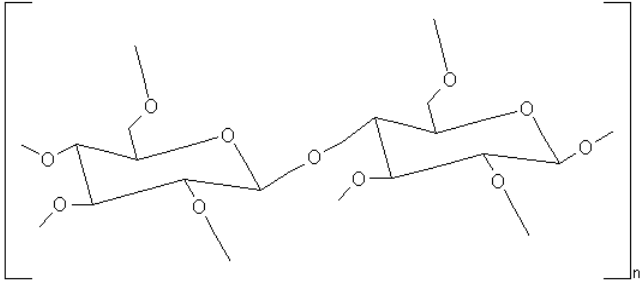
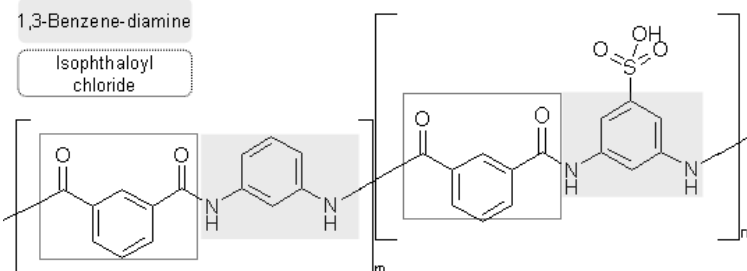
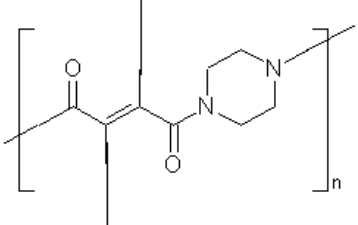
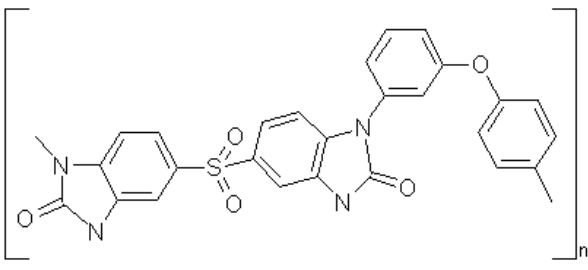
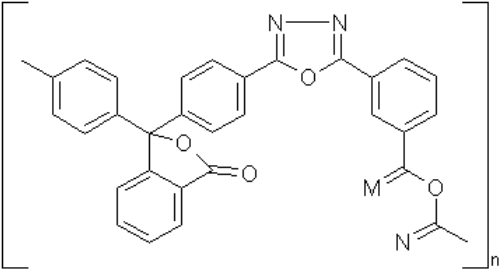
Polymeric RO membranes have dominated commercial applications since the very first RO desalination plant. Due to their technological maturity they offer low-cost fabrication, ease of handling and improved performance in selectivity and permeability. One of the earliest review studies on polymeric RO membrane materials was reported by Cadotte [43]. It focused on composite RO membranes, covering activity from the inception of composite RO membranes up to approximately 1985. In 1993 Petersen [1] offered a comprehensive review of the same subject, focusing on the chemistry of the membrane materials. This section will briefly highlight the early development of membrane chemistry and graphical illustrations are used to visualize the performance improvement of RO membranes. This chronological description provides the readers with a quick overview of RO membranes formed by different mechanisms and their impact on the desalination industry over the years. For a complete study of early RO membrane development, readers are however advised to refer to Petersen [1].

Generally the development of membrane materials can be divided into two periods according to research activity: (i) the search for a suitable material (chemical composition) and membrane formation mechanism (1960s to late 1980s), and (ii) the evolution of more controlled conditions for membrane formulation to enhance membrane functionality and durability (late 1980s to date) [44].

2.1 Early Membrane Chemistry Development and Asymmetric Membrane

In 1949 a report entitled *The Sea as a Source of Fresh Water* initiated research activities on salt-rejecting membranes [45] although initial work on the narrow gap membrane project was not fruitful. In the late 1950s, Reid and Breton reported that a hand-cast thin symmetrical cellulose acetate (CA) membrane could retain salt effectively, achieving 98 % rejection, but that the permeate flux was very disappointing, of the order of $< 10 \text{ mL m}^{-2} \text{ hr}^{-1}$ [46]. Next, the announcement of the Loeb-Sourirajan CA membrane was of historical importance as it first made RO possible in practice [47]. A CA asymmetric membrane was formed with a dense 200 nm thin layer over a thick micro-porous body. This new morphology produced a water flux at least an order of magnitude higher than the initial symmetric membrane [48]. The material molecular composition of these membranes is shown in Table 2.

Table 2. Notable asymmetric RO membranes

Chemical Type & Description	Chemical Structure
<p>1. Cellulose Acetate</p> <p>- Loeb-Sourirajan CA [48]</p> <p>Flux: $0.35 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ Salt rejection: 99 % Test: > 100 bar, 4 % NaCl solution</p>	 <p>The structure shows a repeating unit of cellulose acetate in its cyclic pyranose form. It consists of two glucose units linked by an oxygen atom. Each glucose unit has several hydroxyl groups replaced by acetoxy groups (-O-C(=O)-CH₃). The entire unit is enclosed in brackets with a subscript 'n'.</p>
<p>2. Aromatic Polyamide</p> <p>- Polyamide-hydrazide [49]</p> <p>Flux: $0.67 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ Salt rejection: 99.5 % Test: 30 °C, > 100 bar, 3.5 % NaCl solution</p>	 <p>The structure shows a repeating unit of an aromatic polyamide-hydrazide. It features a central benzene ring connected to two amide groups. One amide group is part of a hydrazide linkage (-NH-NH-C(=O)-) which connects to another benzene ring. The other amide group is part of a standard amide linkage (-NH-C(=O)-) which connects to a third benzene ring. The structure is enclosed in brackets with a subscript 'n'. Labels '1,3-Benzene-diamine' and 'Isophthaloyl chloride' are present near the respective rings.</p>
<p>3. Polypiperazine-amide</p> <p>- [50]</p> <p>Flux: $0.67 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ Salt rejection: 97.2 % Test: > 80 bar, 0.36 % NaCl solution</p>	 <p>The structure shows a repeating unit of a polypiperazine-amide. It consists of a piperazine ring (a six-membered ring with two nitrogen atoms) linked to an amide group (-C(=O)-). The amide group is further linked to a central carbon atom which is also bonded to two other groups. The structure is enclosed in brackets with a subscript 'n'.</p>
<p>4. Polybenzimidazoline</p> <p>- [51]</p> <p>Flux: $0.13 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ Salt Rejection: 95 % Test: > 6 bar, 0.105 % NaCl solution</p>	 <p>The structure shows a repeating unit of a polybenzimidazoline. It features a central benzimidazole ring system (a benzene ring fused to an imidazole ring) which is linked to a sulfonate group (-SO₃⁻). The sulfonate group is further linked to a phenyl ring, which is then linked to a piperazine ring. The structure is enclosed in brackets with a subscript 'n'.</p>
<p>5. Polyoxadiazole</p> <p>- [52]</p> <p>Flux: $0.07 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ Salt Rejection: 92 % Test: > 45 bar, 0.5 % NaCl solution</p>	 <p>The structure shows a repeating unit of a polyoxadiazole. It consists of a central oxadiazole ring (a five-membered ring with two nitrogen atoms and one oxygen atom) which is linked to a phenyl ring. The phenyl ring is further linked to a carbonyl group (-C(=O)-), which is then linked to a piperazine ring. The structure is enclosed in brackets with a subscript 'n'.</p>

Note: The chemical structure shown is a representative segmental structure of this type of material. It does not cover all different variations, *e.g.* the CA structure shown is CDA, although CTA or mixed-CA are grouped into the same category.

Figure 3 highlights the major development of asymmetric RO membrane up to the 1980s. In the decade after the announcement of the Loeb-Sourirajan membrane, further research on CA material was focused on improvement of the membrane transport properties and simplification of manufacturing to bring the technology to industrial application [53]. The cellulose triacetate (CTA) membrane was developed due to a higher stability in a wider range of temperatures and pH, as well as having higher resistance to chemical and biological attack compared to the initial cellulose diacetate (CDA) material. However, CTA is prone to compaction resulting in severe loss of flux even at moderate operating pressures of 30 bar or less [54]. A blend of CDA and CTA finally offered higher permeability and selectivity than CA membranes, as well as offering higher resistance to compaction [55]. More studies have been performed, such as control degree of mixed ester substitution for the hydroxyl groups of the cellulose to monitor the performance of the CA membranes [56].

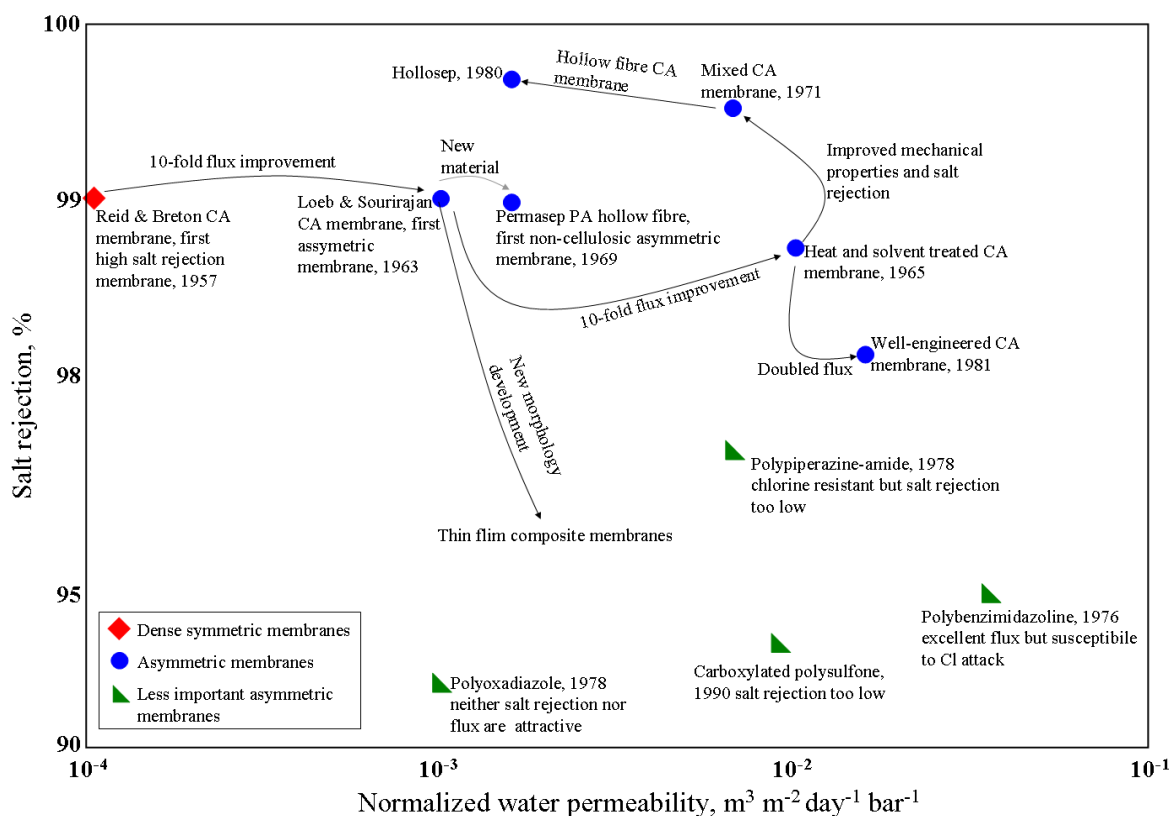


Figure 3. The development of asymmetric RO membrane

Although there was an intensive search for alternative membrane polymers, CA remained the best membrane material for RO until 1969. However, the susceptibility of the acetate group to hydrolysis in both acidic and alkaline conditions, as well as sensitivity to microbial contamination, limited durability and the range of applications [57]. Thus, a stronger material with higher chemical stability was obviously needed and although many alternative polymers were tested in the 1960s the resulting improvements were insignificant.

The first non-cellulosic asymmetric membrane to gain attention was developed by Richter and Hoehn and consisted of an aromatic polyamide (PA) asymmetric hollow-fibre membrane [58]. This was subsequently commercialised by Du Pont under the trade name of B-9 Permasep®, for application in brackish water desalination. Though it has relatively low flux and salt rejection, the durability, stability and versatility are greater than CA or aromatic polyhydrazides [59]. Despite the low flux, its commercial success can be attributed to the highly effective packing of the hollow fibres, which outperformed the CA spiral wound elements in terms of flux per unit module volume. For detailed discussion about the variation in reactants for PA asymmetric membrane, readers are referred to [60].

However the susceptibility of polyamides to attack by disinfectants such as chlorine (halogens) and ozone was observed after the prolonged use of the B-9 Permasep® membrane. Chlorine-resistant asymmetric membranes based on polypiperazine-amides have subsequently been developed (Table 6) [50, 61, 62]. They have comparable permselectivity to the asymmetric CA membrane. The reduced presence of amidic hydrogen also improves the resistance to chlorine attack [63]. However, this membrane was not commercialised due to its relatively low salt rejection ($\leq 95\%$) [64]. The presence of the sulphonic and phenyl groups in sulfonated polysulfone was expected to enhance permeability, mechanical, chemical and biological stability however the salt rejection was below the acceptable level required to be commercialised [65]. Similarly, carboxylated polysulfone which gives a promising flux also suffers from uncompetitive salt rejection [66, 67]. While polybenzimidazoline (PBIL) membranes developed by Teijin show excellent permselectivity even in harsh operating conditions, they are susceptible to pressure compaction and chlorine attack [51, 68, 69]. In contrast, polyoxadiazole is found to have superior mechanical and temperature stability but its salt rejection and permeability is not commercially attractive for RO applications [52, 60].

2.2 Thin Film Composite (TFC) Membrane

Only a few soluble polymers can form asymmetric structures in one-step casting, and even less are commercially attractive in terms of the right combination of permeability and salt rejection. In addition, under pressure, the CA asymmetric membrane experienced densification in the middle transition layer [70]. This led to two-step casting methods that enabled individual optimization of the materials used for the micro-porous support film and for the barrier layer, the former for mechanical support and the latter for optimal salt rejection and permeate flux. Furthermore, a wide variety of polymers can be tested for the barrier layer and support layer separately. These anisotropic membrane morphologies are now referred to as composite membranes.

2.2.1 Early Development of TFC Membrane

As shown in Figure 4, Francis casted the first TFC membrane by float-casting a CA ultra-thin film on the water surface followed by annealing and lamination onto a pre-formed CA microporous support [71]. Membranes produced with this technique never gained commercial interest because their asymmetric counterparts offered a better flux for lower manufacturing costs. After an extensive empirical study, polysulfone was found to be the optimum material for the support layer due to its resistance to compaction, reasonable flux and most importantly, its stability in an acidic environment which enables further development of the TFC membrane by acid polycondensation and interfacial polymerisation [72].

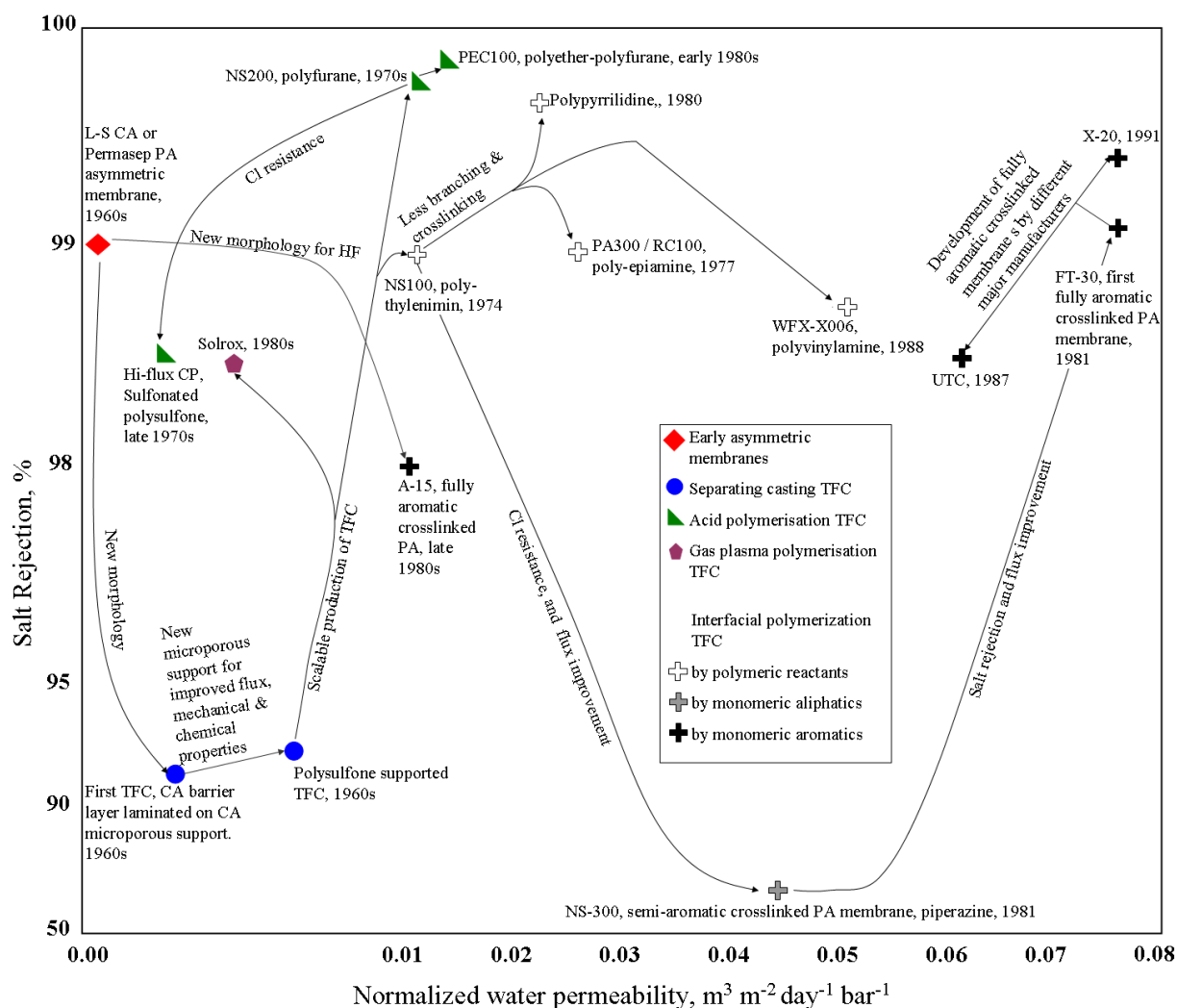


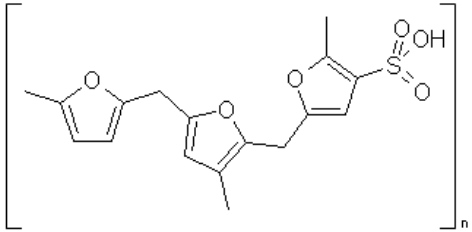
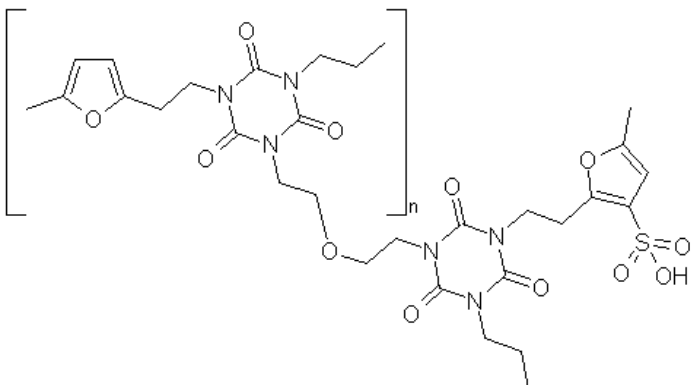
Figure 4. The development of thin film composite RO membrane

A dip-coating method involving acid polycondensation of low-molecular-weight hydroxyl-containing compounds was proposed to overcome scaling up problems in float-casting technology [60, 73]. The first patented product based on this concept was named NS-200, a product of reaction of furfuryl alcohol, sulphuric acid and polyoxyethylene (Table 3) [74]. It showed excellent salt rejection but suffered from irreversible swelling and hydrolysis of the sulphate linkage. Another membrane prepared by acid polycondensation was the PEC-1000 TFC RO membrane produced by Toray Industries, Inc., [75]. It used 1,3,5-tris(hydroxyethyl)isocyanuric acid instead of polyoxyethylene. Despite its extremely high salt and organic compound rejection with adequate flux, it was susceptible to chlorine attack. Sulfonated polysulfone membranes have been developed due to their stability in oxidizing environments [65]. Nevertheless, strong Donnan effects were observed, implying the

shielding effect of divalent cations can significantly decrease the monovalent ion rejection. A summary of notable TFC RO membranes is shown in Table 3.

The barrier layer can be formed by plasma polymerization, where fragmentation of monomer vapour is induced by the energy of the gas plasma, and atomic polymerization is propagated onto a cool surface, often a polysulfone support. A range of polymers have been tested and good permselectivity can be obtained from vinylene carbonate / acrylonitrile, vinyl acetate / acrylonitrile, allylamine, acetylene / water / nitrogen, acetylene / water / carbon monoxide combinations [76-82]. Yasuda's group was particularly active in plasma polymerization and a membrane formed by acetylene, water and nitrogen performed particularly well in sea water desalination test, with 99 % salt rejection for a flux of $1.5 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ at 100 bar operation. Despite research into plasma-polymerized films and application in gas separation [83], only one RO membrane manufactured using this technique has been commercialized, namely the Solrox membrane. Plasma polymerized RO membranes mostly have low chlorine resistance due to their nitrogen-enriched chemical structure.

Table 3. Notable TFC RO membranes

Chemical Type & Description	Chemical Structure
<p>1. Polyfurane</p> <p>- Name: NS-200</p> <p>- [74]</p> <p>Flux: $0.8 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$</p> <p>Salt Rejection: 99.8 %</p> <p>Test: > 100 bar, 3.5 % NaCl solution</p>	
<p>2. Polyether-Polyfurane</p> <p>- Name: PEC-1000</p> <p>- [75]</p> <p>Flux: $0.5 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$</p> <p>Salt Rejection: 99.9 %</p> <p>Test: > 69 bar, 3.5 % NaCl solution</p> <p>-Excellent organic rejection</p>	

3. Sulfonated Polysulfone

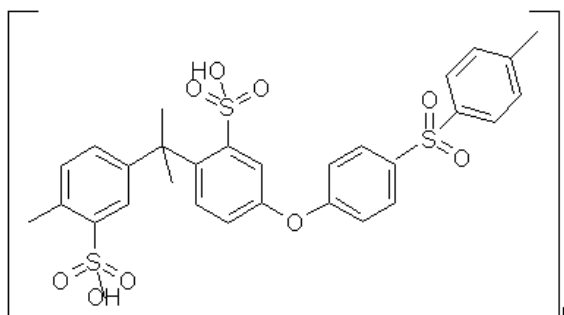
- Trade Name: Hi-Flux CP
- [84]

Flux: $0.06 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$

Salt Rejection: 98 %

Test: > 69 bar, 3.5 % NaCl solution

-Excellent chlorine resistance



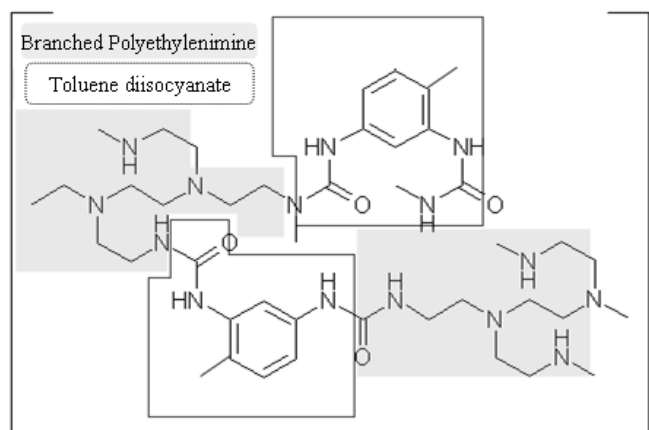
4. Polyamide via polyethylenimine

- Name: NS-100
- [22]

Flux: $0.7 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$

Salt Rejection: 99 %

Test: > 100 bar, 3.5 % NaCl solution



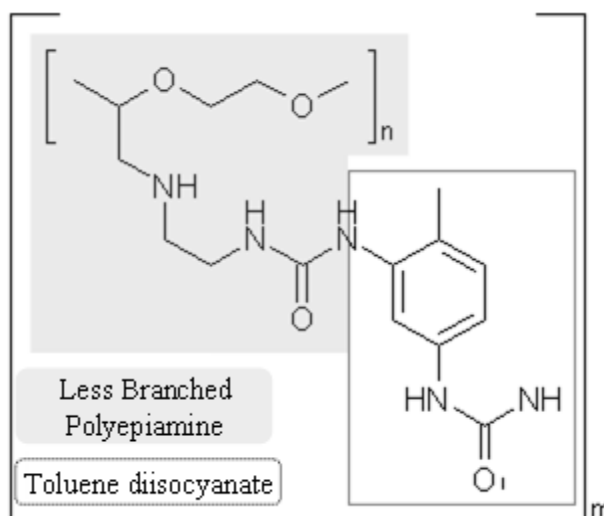
5. Polyamide via polyepiamine

- Trade Name: PA-300 or RC-100
- [85]

Flux: $1.0 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$

Salt Rejection: 99.4 %

Test: > 69 bar, 3.5 % NaCl solution



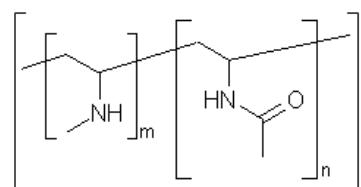
6. Polyvinylamine

- Trade Name: WFX-X006
- [86]

Flux: $2.0 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$

Salt Rejection: 98.7 %

Test: > 40 bar, Conductivity = $5000 \mu\text{S cm}^{-1}$



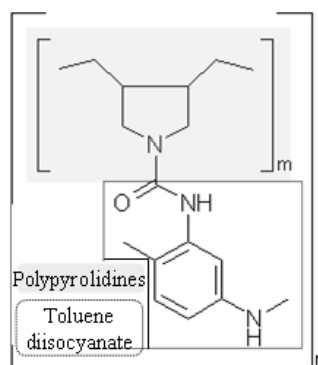
7. Polypyrrolidine

- [87]

Flux: $0.8 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$

Salt Rejection: 99.7 %

Test: > 40 bar, 0.5 % NaCl solution



8. Polypiperazine-amide

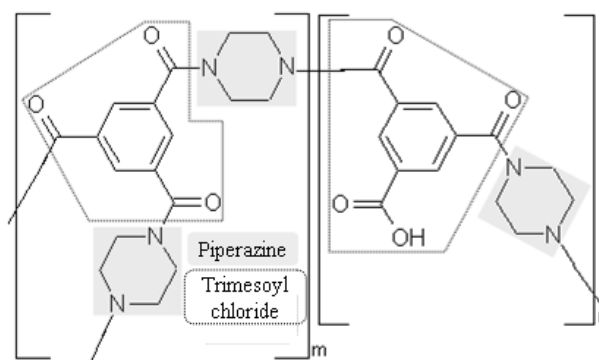
- Name: NS-300

- [88]

Flux: $3.3 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$

Salt Rejection: 68 %

Test: > 100 bar, 3.5 % NaCl solution



9. Crosslinked Fully Aromatic Polyamide - 1

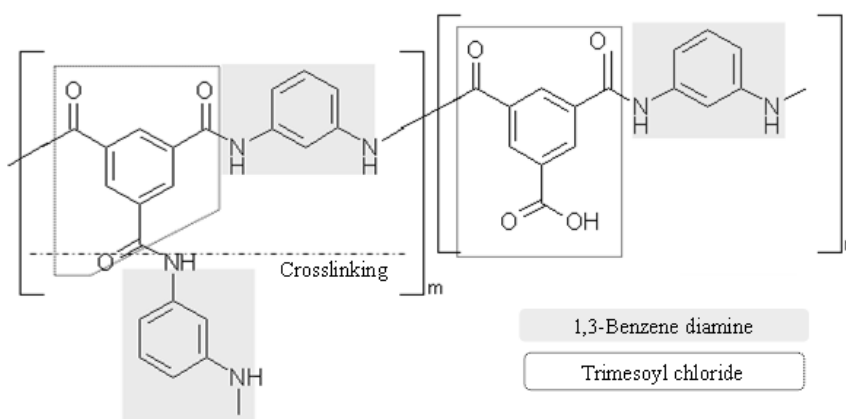
- Trade Name: FT-30

-[89]

Flux: $1.0 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$

Salt Rejection: 99 %

Test: > 15 bar, 0.2 % NaCl solution



10. Crosslinked Fully Aromatic Polyamide - 2

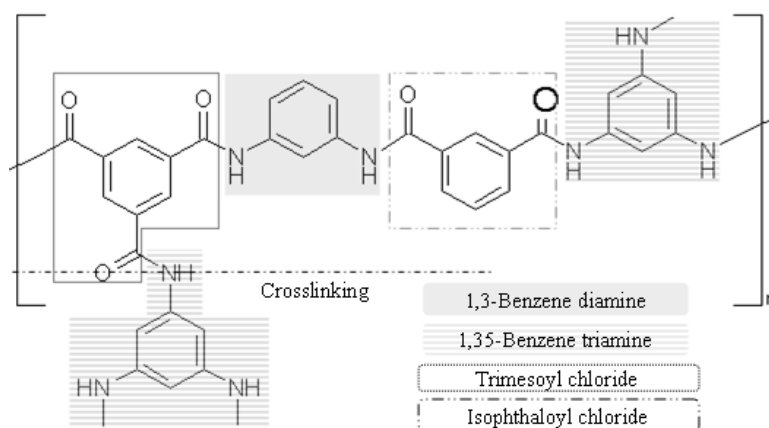
- Trade Name: UTC series

-[90]

Flux: $0.8 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$

Salt Rejection: 98.5 %

Test: > 15 bar, 0.5 % NaCl solution



and a salt rejection 99.4 % at 70 bar, as compared to NS-100. This enhancement has led to PA-300 spiral wound modular elements being installed in the TFC SWRO plant at Jeddah [97]. On the other hand, RC-100 has a high resistance to bio-fouling which has resulted in successful installation at Umm Lujj II and other desalination plants [98]. There are two other noteworthy interfacially polymerised TFC membranes from polymeric reactants, namely polyvinylamine that offers high flux and polypyrrolidine whose amino/carboxy-groups can be controlled to vary amphotericity and selectivity.

Initial attempts at interfacial polymerization of monomeric amines, including both aliphatic and aromatic diamines, with terephthaloyl chloride, did not produce membranes with attractive salt rejection performance [1]. Cadotte revisited this case and optimised the polymerisation conditions [61-62, 99]. Nevertheless, this polypiperazine-amide membrane exhibits strong Donnan exclusion effects due to the anionic charged surface via the presence of carboxylic groups, *i.e.* it can achieve excellent rejection of divalent anions such as sulphate at high flux. This makes it sufficiently attractive for practical usage in nanofiltration (NF) and the membrane has been designated as NS-300 (Table 3). A range of NF membrane based on similar chemistry have been commercialised, e.g. NF-40 series by DOW FILMTEC™ [88], NTR-7250 by Nitto Denko [100], UTC-20 by Toray Industries [101].

Cadotte discovered that membranes with excellent permselectivity can be produced using monomeric aromatic amines and aromatic acyl halides containing at least 3 carbonyl halide groups, with trimesoyl chloride giving the best results [89, 102, 103]. Unlike other interfacial polymerization methods, heat curing was avoided, and acid acceptor and surfactants were not required because polymerisation and crosslinking were both rapid even when acyl halide was supplied at lower concentrations. Membrane FT-30 (Table 3) was prepared by interfacial reaction between 1,3-benzenediamine with trimesoyl chloride, producing a very unique surface characteristic, which has been described as a ‘ridge and valley’ structure, rather than the smooth or slightly grainy surface obtained from aliphatic amines [21]. Studies have shown that this rough ‘ridge and valley’ surface feature is closely related to the increased effective surface area for water transport and thus water flux [104]. In seawater desalination tests, FT-30 yielded fluxes of nearly $1 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$, with 99.2 % salt rejection operating at 55 bar. The aromatic polyamide structure of FT-30 provides a high degree of resistance to compression, thermal and chemical resistance, as well as a wide pH operating range. Although not completely resistant to chlorine attack, FT-30 shows a degree of tolerance to chlorine which is sufficient to withstand accidental exposure to this chemical [105], and a series of products based on this membrane have been commercialised by DOW FILMTEC™

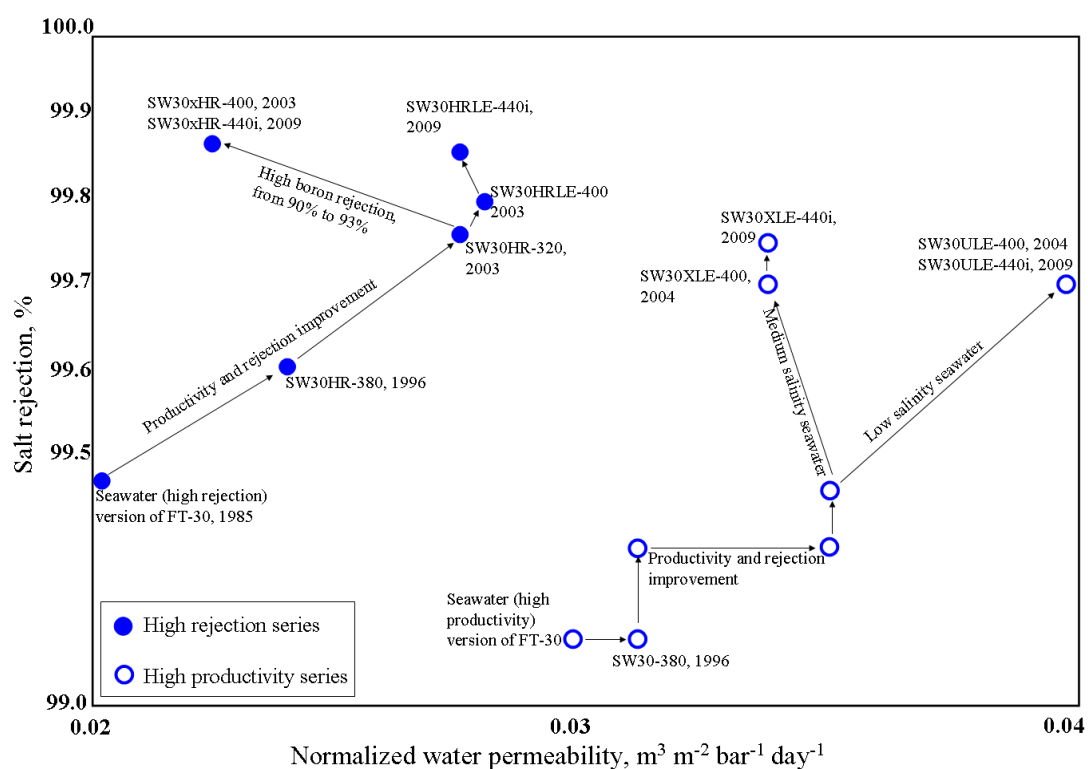
[106]. Crowds has concluded that this membrane has significant impact on the design and cost of RO desalination [107]. It was the first spiral wound membrane element capable of competing with the Du Pont asymmetric hollow fibre polyamide B-9 Permasep® membranes, originally released in 1972. The success of FT-30 led to the release of a number of similar products [108], e.g. CPA2 membrane produced by Hydranautics [109], UTC-70 by Toray Industries [110]. Permasep A-15 TFC membrane (Table 3) prepared by reacting 1,3-benzenediamine with saturated cross-linking agent, cyclohexane-1,3,5-tricarbonyl chloride resulting an aralkyl polyamide membrane gives better flux. [91, 111]. Sundet also patented the use of isocyanato aromatic acyl halides (*e.g.* 1-isocyanato-3,5-benzenedicarbonyl chloride) as cross-linking agents for 1,3-benzenediamine, in order to produce a membrane containing both amide and urea linkages that excels in both flux and salt rejection (Table 8) [92]. This latter membrane was designated X-20, showing superior resistance to fouling and chlorine due to its relatively neutral surface charge and stronger polyamide-urea bond linkage [112].

2.3 Membrane Post-Synthesis Modifications and Control of Interfacial Polycondensation Reactions

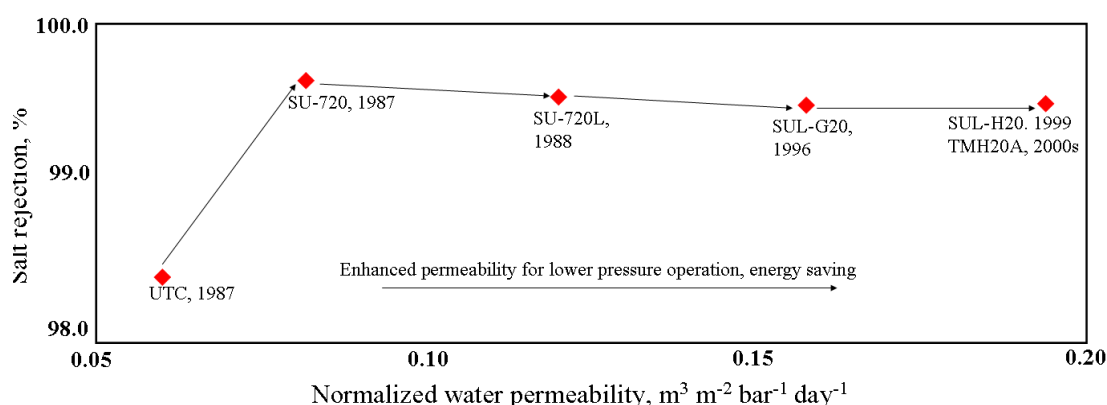
After the revolutionary success of the introduction of cross-linked fully aromatic polyamide TFC RO membranes into the market, research and development towards new polymeric materials for RO membranes has declined dramatically. Current products from major manufacturers of RO desalination membranes are still based on the original chemistry discovered during the 1980s, *i.e.* interfacial polymerisation of monomeric aromatic amines. The biggest manufacturer of desalination membranes, DOW FILMTEC™, currently sells products based on FT-30; membranes supplied by Toray are based on UTC-70; Hydranautics membranes are based on NCM1, which is identical to CPA2; and Trisep membranes are based on X-20. On the other hand, asymmetric membrane products are still based on the conventional CA materials, for example the Toyobo HoloSep™ range of products is based on CTA and is the dominant asymmetric RO membrane.

Despite the fact that no new polymeric membranes has been commercialized recently, the performance of RO membranes has still improved dramatically (Figure 5), *i.e.* water permeability has been at least doubled, and the recovery of fresh water can be over 60 %. These improvements are the results of surface modification, and closer monitoring of interfacial polymerization reaction parameters, as well as more effective design of the module structure [41, 113, 114]. In addition, better understanding of, and insight into, the membrane

structure, associated with advancements in membrane characterization techniques, has undoubtedly played an important role [115]. For example, the use of Atomic Force Microscopy (AFM) has been a useful tool which has confirmed that surface roughness of a membrane can greatly enhance permeability, whilst at the same time maintaining high salt rejection due to the increase in effective membrane area [116].



(a)



(b)

Figure 5. The development of RO membrane by reaction optimisation and post-synthesis surface modifications: (a) Dow Filmtec seawater series and (b) Toray brackish water series.

It has been difficult to track post-1990 development of commercially important RO membrane due to greatly reduced patenting activity by membrane manufacturers. To reveal the chemical composition and post-treatment that has been performed on commercial RO membranes, researchers have been combining the use of various analytical techniques. Rutherford back scattering spectrometry is a powerful tool for elemental composition analysis at different layers and physicochemical characterisation [117-120]. A combination of various analytical techniques, XPS, ATR-FTIR, TEM, and streaming potential measurement has also been used to gain understanding of both physical and chemical structure of the membrane and how it relates to the membrane performance [121-123]. Cahill et al. has reviewed the use of various analytical tools for membrane characterisation [124].

While there are proactive academic research activities in this field, this review focused on the most influential engineering developments that have been adapted into commercial products. For a more complete review of academic research activities on surface modification of TFC membranes readers are directed to [2].

2.3.1 Surface Modification

A major area of membrane post-treatment research involves hydrophilization, which can give an increase in permeability and chlorine resistance. Although there has been some success at synthesizing membranes with incorporated hydrophilic groups (such as carboxylate) and eliminating amidic hydrogen, the monomer reactants used are not readily available and the preparation method is too complex [125-128]. Therefore post-treatment to chemically modify the membrane surface properties is preferred, and various chemical and physical techniques have been developed. Various water soluble solvents such as acids and alcohols have been used to treat the membrane surface. Mixtures of alcohol (ethanol and isopropanol) and acid (hydrofluoric and hydrochloric acid) in water are also used to improve flux and rejection due to the partial hydrolysis and skin modification initiated by the alcohol and acid [129]. The presence of hydrogen bonding is claimed to encourage interaction between acid and water, which produces more surface charge and eventually enhances the hydrophilicity and water flux remarkably. Mickols patented post-treatment of a membrane surface with ammonia or alkyl compounds, particularly ethylenediamine and ethanolamine, and achieved both enhanced flux and salt rejection [130]. A 70 % flux improvement is attained by soaking composite membranes in solutions containing various organic species, *e.g.* glycerol, sodium lauryl sulphate, and the triethylamine salt of camphorsulfonic acid [131,

132]. Post-treatment of membranes using an aqueous solution of poly (vinyl alcohol) and a buffer solution can effectively improve the abrasion resistance as well as flux stability of the membrane [133, 134].

Hydrophilization has also been achieved by coating the membrane surface with more hydrophilic compounds. As mentioned in reference [2], coatings have been the preferred method to tackle fouling issues. One important example is the launching of Hydranautics LFC series in 1996 [135], and the recent introduction of LFC3-LD in 2005 [136] targeting applications in wastewater treatment/reclamation. Neutrally charged, these membranes are designed to minimise the adsorption of organic foulants. Their reported stable performance over time has been [137] attributed to a poly(vinyl alcohol) (PVA) coating on the surface of conventional fully aromatic polyamide membrane [122]. Coatings of PVA and poly(N,N-dimethylaminoethyl methacrylate) have also shown superior resistance against chlorine attack [123, 138]. Recently hydrophilic dendritic polymers have been reported to have successfully modified a membrane surface to reduce fouling effects [139, 140].

Dramatic flow enhancement was achieved by a chemical treated FT-30 membrane (ref). The membrane was soaked in a 15 % solution of hydrofluoric acid for seven days and exhibited about a 4-fold improvement in flux and slightly higher salt rejection. Membrane surface analysis showed that the fluorine ratio had been increased as a result of the treatment (Kah Peng, why is this significant?). In addition, etching of the surface had resulted in a thinner barrier layer [141]. Whilst increasing the flux without altering the chemical structure, this method however suffers from leaching of the hydrophilizing components over time causing the loss of any flux enhancement [142].

Other surface modification techniques including the use of free radical-, photochemical-, radiation-, redox- and plasma-induced grafting, are currently used to covalently attach some useful monomers onto the membrane surface which has been covered in [2]. Gas plasma treatment is also used to induce surface modification: water permeability is improved by oxygen plasma treatment due to the introduction of hydrophilic carboxylate groups, whereas argon plasma treatment can greatly enhance chlorine resistance by increasing the extent of cross-linking at the nitrogen sites [143, 144]. Recently, Li et al. reported that the use of atmospheric gas plasma surface activation and graft polymerisation on the surface of conventional polyamide TFC membranes can greatly enhance anti-fouling properties [145]. After gas plasma surface activation, a polymeric brush layer is formed by free radical graft polymerisation using methacrylic acid or acrylamide monomers. This brush layer can effectively reduce the ability of foulants to adhere to the surface, as proven in various fouling

tests where this membrane has outperformed the commercial low-fouling membrane LFC1, particularly in mineral fouling test. In addition, both atmospheric gas plasma treatment and graft polymerisation are readily adaptable to large scale membrane manufacture.

2.3.2 Optimisation of Polymerisation Reactions

Another area of intense research study is the optimization of interfacial polymerisation reaction mechanisms, including kinetics, reactant diffusion coefficients, reaction time, solvent solubility, solution composition, nucleation rate, curing time, polymer molecular weight range, and characteristics of the micro-porous support [146-150]. The early success of Tomaschke [109] and Chau [151] in using additives in the casting solution (amine reactants) has led to intensive research in using different species of additives. The use of amine salt such as the triethylamine salt of camphorsulfonic acid, as an additive in the aqueous amine reaction solution enables post-reaction drying at temperatures higher than 100 °C. As a result a more cross-linked membrane is formed with an improvement of the salt rejection without compromising the flux. Chau added polar aprotic solvents, especially N,N-dimethylformamide, into the casting solutions which eventually gives higher residues of carboxylate content and thus increased water permeability.

The inclusion of additives into the casting solution plays a major role in alteration of monomer solubility, diffusivity, hydrolysis, protonation, and they can also act to scavenge inhibitory reaction byproducts [149]. Many patents disclose that the addition of alcohols, ethers, sulphur-containing compounds, water soluble polymers, or polyhydric alcohol to the amine solution can improve membrane permeability without significant change in salt rejection [152-156]. For example, miscibility of water and hexane is improved by the addition of dimethyl sulfoxide into the casting solution and diffusion of the monomer amine reactants is also enhanced. This enables the formation of a thinner barrier layer and hence water flux is improved [157]. Figure 6 shows micrographs of RO membranes produced using different additives which result in different permselectivities, from Kwak *et al.*, 1999 [158].

Instead of mixing additives into the amine reactant solutions, Mickols patented the addition of a 'complexing agent' into the acyl chloride (normally trimesoyl chloride) solution. Most widely used are phosphate-containing compounds such as triphenyl phosphate, which can modify and eliminate the repulsive interaction of acyl chloride with other compounds by removing the halides formed during amide bond formation. This minimises the concurrent

hydrolysis and allows sufficient reaction between the acyl halide and amines to take place for enhanced membrane formation, in particular permeate flux is increased [159, 160].

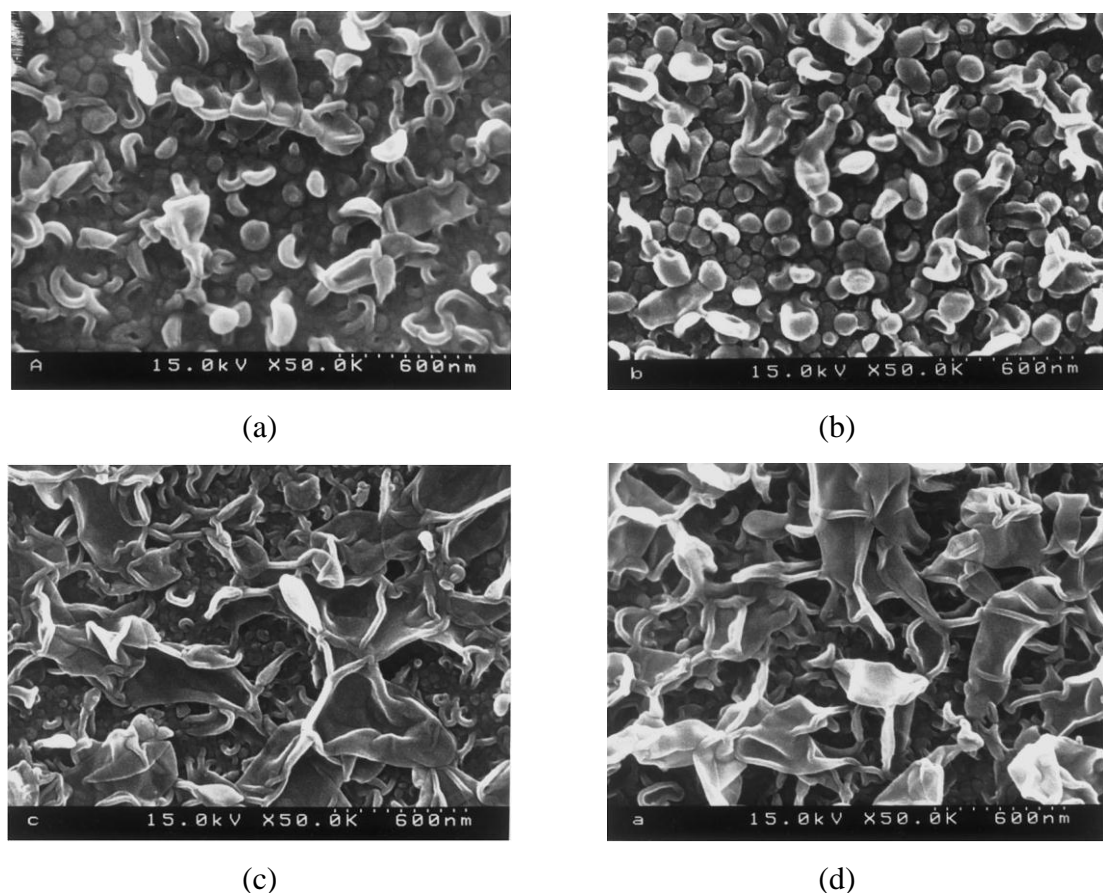


Figure 6. FE-SEM micrographs of RO membranes surface of various permselectivity.

(a) Flux: $1.15 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$, Salt rejection: $> 96 \%$.

(b) Flux: $1.16 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$, Salt rejection: $> 99.1 \%$.

(c) Flux: $1.52 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$, Salt rejection: $> 98.7 \%$.

(d) Flux: $1.85 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$, Salt rejection: $> 98.4 \%$.

(Reprinted with permission from Kwak *et al.*, 1999) [158]

Note: Tested at 20°C , > 15 bar for 0.2% NaCl solution. Scale bar is 600 nm for all figures.

Recently the introduction of active additives, more specifically surface-modifying macromolecules, into the reactants has been reported. In this method the additive can move toward the active surface during the polymerization, and hence alter the surface chemistry to obtain desirable properties. For example, the participation of hydrophilic surface-modifying macromolecules, such as poly(ethylene glycol) end-capped oligomers, in the interfacial

polycondensation reaction has improved the membrane flux and stability of salt rejection over time [23].

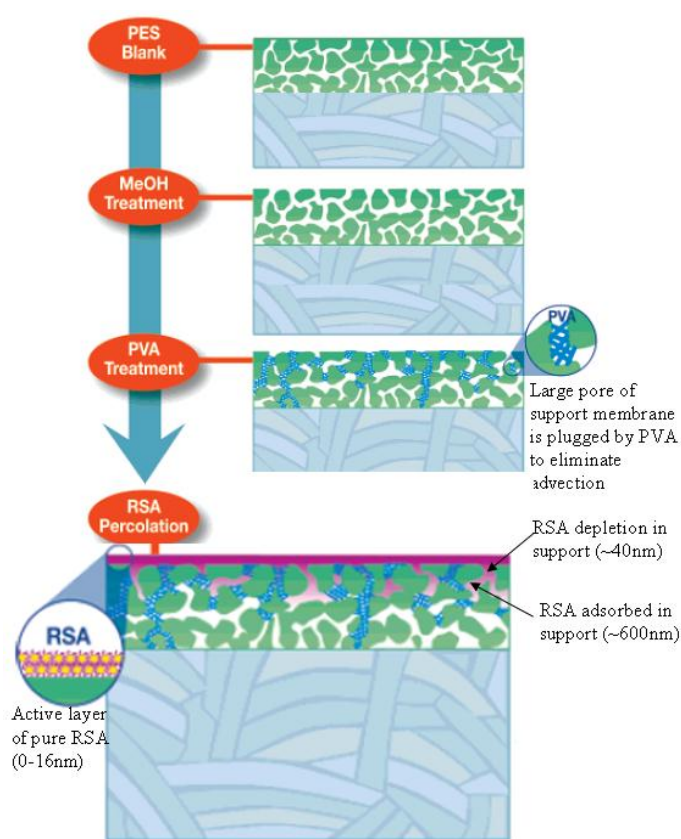
3. Novel Desalination RO Membranes

Since the operation of the first RO desalination plant, only polymeric membranes have been employed for industrial use. As shown in Figure 5, the advances in conventional polymeric RO membrane has been rather limited since the late 1990s, especially the membrane permeability. Though more membrane modules have been released, most of them are improved by increasing membrane area per module. Recently, advances in nanotechnology have led to the development of nano-structured materials which may form the basis for new RO membranes. Li and Wang have included inorganic membranes and thin film nano-composite membranes in a recent review whereas Mauter and Elimelech have discussed the perspective of carbon nanotube membranes as high flux filters [2, 161]. In this section, the development of membranes that have been discussed in the previous two reviews will be briefly highlighted with a focus on their possibility to be engineered into commercial RO membranes. At the same time, discussion about structured polymeric membrane synthesized via a new route, carbon-derived nanoporous membranes and biomimetic membrane are included. The coverage of all proposed novel desalination RO membranes in this section is aimed to provide a general overview of these materials and to draw a fair comparison to their possibility to be developed into commercial RO membranes.

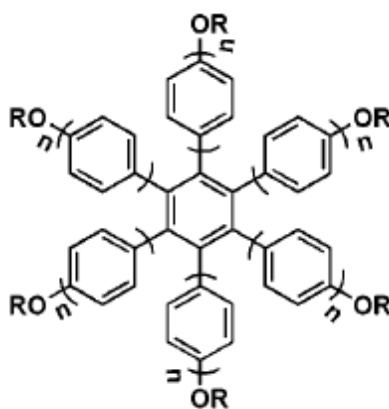
3.1 Polymeric Membrane by Rigid Star Amphiphiles

A nanofiltration membrane based on rigid star amphiphiles (RSA) has been reported recently [162, 163]. As illustrated in Figure 7(a), the membranes were prepared by direct percolation of methanol solutions of the RSAs through an asymmetric polyethersulfone support that had been previously conditioned with methanol and cross-linked poly-vinyl alcohol. Figure 7(b) shows one of the RSA molecules that were synthesized by various cyclization approaches as membrane building block materials. In SEM and AFM analysis, this membrane has shown extremely smooth surface, with an average roughness in the range of 1-2 nm as compared with higher values for commercial NF membranes (20-70 nm). The RSA membrane barrier layer is ultra-thin, with a thickness of about 20nm. The composite multi-layer dendrimer structure allows the control of narrower pore size distribution. In

respect to commercial NF membranes, these membranes showed comparable contaminants rejection performance with double the flux. Considering the similarity of polymeric NF and RO membrane morphology, this new route of polymeric membrane synthesis may offer a better alternative in tuning membrane structure. However, further investigation is needed to verify the suitability for RO process; in particular its salt rejection is yet unknown.



(a)



(b)

Figure 7 (a) RSA membrane synthesis process (Adapted from Lu *et al.*, 2007) [162]

(b) One of the RSA molecules tested in [162]

3.2 Ceramic / Inorganic Membranes

Ceramic membranes are mostly made from alumina, silica, titania, zirconia, or any mixture of these materials. Due to the high manufacturing cost, use is currently limited to applications where polymeric membranes cannot be used, *i.e.* high operating temperatures, radioactive / heavily contaminated feeds, and highly reactive environments [164]. Generally ceramic membranes are made up of a macro-porous support layer and a meso- or micro-porous active layer. The state of the art ceramic membrane preparation techniques include paste extrusion for supports, and slip-casting of powder suspensions or sol-gel processing of colloidal suspensions for deposition of the active layer. Membrane elements have been developed from simple tubular modules to monolithic honeycomb-type structures which offer higher packing efficiency. Currently commercial ceramic membranes are widely used in micro- and ultra-filtration applications whereas ceramic membranes for nano-filtration are under development [165].

The industrial use of ceramic membranes in domestic water production is rare but their process robustness has attracted the attention of researchers for both membrane distillation [166, 167] and pervaporation [168]. Early results on the use of ceramic membranes for RO desalination have recently been reported by a group of researchers from the New Mexico Institute of Mining and Technology [169]. Given the potential of desalting oil field water, and being motivated by molecular dynamic simulation results showing 100 % of ion rejection by perfect all-Si ZK-4 zeolite membranes [170], this group has experimentally investigated the RO separation mechanism and feasibility of application of ceramic membranes. Figure 8 shows the sub-nm inter-crystalline pores within the zeolite structure that allow the passage of water molecules and reject the salt [171].

Theoretical calculations have shown that ions can be completely excluded by zeolite membranes with pore sizes smaller than the size of the hydrated ion. A-type zeolite membranes exhibit 0.4 nm pores and MFI-type membranes 0.56 nm. The first experimental attempt at RO of a NaCl solution using a MFI silicalite-1 zeolite membrane showed 77 % salt rejection and a water flux as low as $0.003 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ at 21 bar. It is also reported that rejection of bivalent cations is higher than for monovalent ions, in a test using a feed containing mixed ion species. In other words the rejection of sodium ions in a mixed ion

solution is lower than that for a pure solution of NaCl. These results show that the filtration mechanism is not only dependent on size exclusion, but also on Donnan exclusion due to the charged double layer induced by adsorbed ions on the pore or the intercrystalline walls [172].

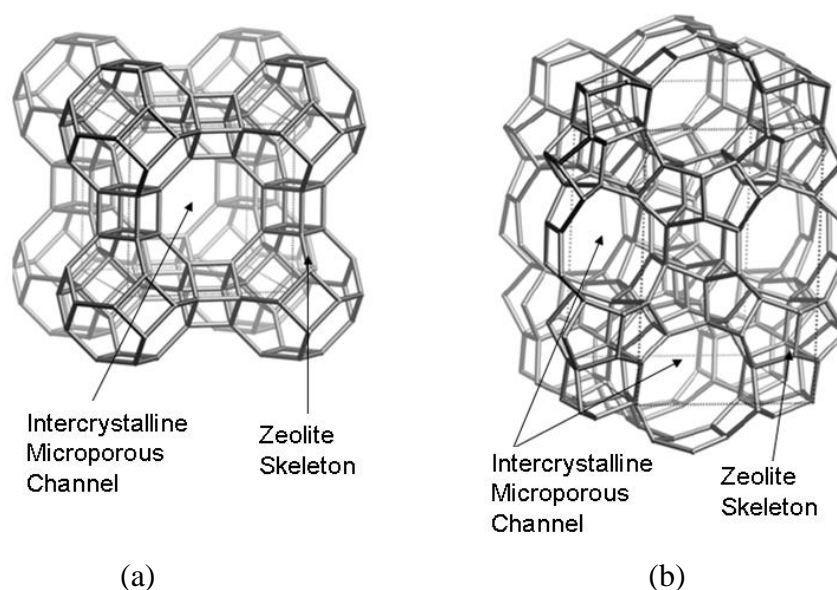


Figure 8. Micro-porous ceramic membrane structure: micro-porous channel in the crystalline structure (a) Type A Zeolite; and (b) MFI Zeolite.

(Reprinted with permission from Baerlocher *et al.*, 2007) [171]

Although the first RO test with a zeolite membrane was unsuccessful, *i.e.* both salt rejection and water flux were too low to be of practical use, subsequent work has been conducted to improve both by modifying the zeolite structure. The Si / Al ratio, which dominates the wettability and membrane surface charge, has been optimised to give improved flux and salt rejection. The Al content in the membrane can alter the surface hydrophilicity and therefore affinity with water [173]. Defects in the crystal structure are minimised by secondary growth of a zeolite layer on zeolite seeded onto a porous α -alumina substrate [174]. This combined effort generated a remarkable improvement, with a 2 μm thick zeolite membrane with 50 : 50 Si / Al ratio rejecting 92.9 % of sodium ions with a water flux of 1.129 $\text{kg m}^{-2} \text{h}^{-1}$ at 28 bar [175]. In a recent report from the same group, the thickness of the membrane has been further reduced to 0.7 μm , providing excellent organic (> 99 %) and salt rejection (97.3 %) as well as nearly 4 times improvement in water flux [176, 177].

Though the improvement of zeolite membranes has been tremendous in the past 10 years, their performance and economics are still no match for polymeric membranes. The zeolite membrane thickness is still at least 3 times higher than current state of the art polymeric RO

membranes, causing higher resistance to water flux. Consequently ceramic membranes require at least 50 times higher membrane area than polymeric ones to achieve an equivalent production capacity. This value can be even higher when the higher density and lower packing effectiveness are considered. Moreover, whilst zeolite membranes are claimed to have high organic rejection, organic fouling has caused almost 25 % loss in flux after only 2 hours of operation, though full recovery of flux was achieved after chemical washing [177].

Feeds of higher salinity are expected to cause shrinkage of the double layer due to the screening effect of counter ions on the surface charge. Hence, an undesirable increase in effective inter-crystalline pore size would facilitate ion transport and therefore reduce rejection efficiency. These tests were carried out with a low NaCl concentration (0.1 %) and standard seawater desalination tests at 3.5 % NaCl should be investigated to evaluate potential usage for desalting oil field seawater.

Carbon is another candidate for formation of sub-nm porous material. Controlled pore size distribution of carbide derived carbon (CDC) materials has been reported [178]. CDC offers good control of pore size, shape and uniformity, for example via manipulation of chlorination temperature as shown in Figure 9. The synthesis of CDC membranes by formation of a thin CDC film on top of a porous ceramic support has been reported [179]. This preliminary study introduces a route to producing asymmetric CDC membranes with average pore sizes of about 0.7 nm, showing a potential for monovalent salt exclusion. Nevertheless, further research is necessary to test the feasibility and practicality of CDC membranes for RO desalination.

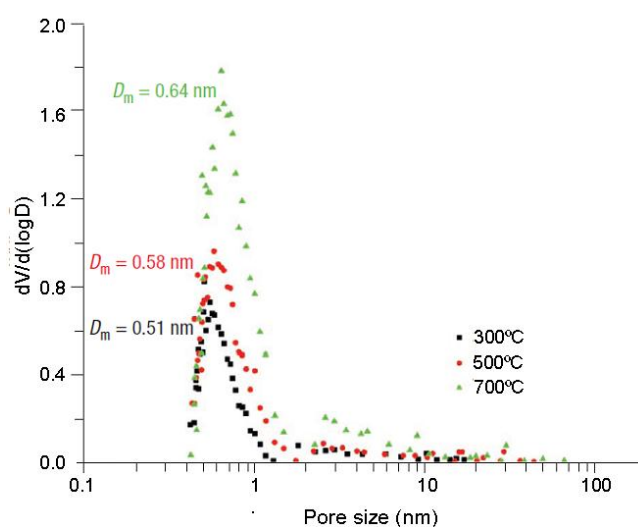


Figure 9. Differential pore size distribution for CDC synthesized membrane at different chlorination temperature measured by methyl chloride adsorption (Reprinted with permission from Gogotsi *et al.*, 2003) [178].

3.3 Mixed Matrix Membranes (MMM)

The concept of MMM, the combination of organic and inorganic material, is not new. UOP developed a silicalite-cellulose acetate MMM for gas separation in 1980, showing superior selectivity to conventional polymeric membranes [180]. Despite the fact that MMMs have been developed for water / ethanol separation via pervaporation in 1990s, the incorporation of inorganic materials into organic RO TFC membranes only started in the early 2000's [181]. The main objective of MMM is to combine the benefits offered by each material, *i.e.* the high packing density, good permselectivity, and long operational experience of polymeric membranes, coupled with the superior chemical, biological and thermal stability of inorganic membranes [182].

3.3.1 Nano-particle / Polymeric Membranes

Titanium oxide (TiO_2) is a well known photocatalytic material, widely used for disinfection and decomposition of organic compounds [183], and these properties make it interesting as an anti-fouling coating. Anatase TiO_2 nano-particles (< 10 nm) have been prepared by the controlled hydrolysis of titanium tetra-isopropoxide. These were subsequently dip-coated onto an interfacially polymerized fully cross-linked polyamide TFC membrane with a surface layer functionalised with carboxylate groups [184]. The carboxylate groups are necessary for the self-assembly of TiO_2 within the barrier layer via an adsorption mechanism. Testing with *E. coli*-containing feed water has shown superior anti-bio-fouling properties, especially with the aid of UV excitation, without compromising the flux and salt rejection performance of the original membrane. No significant loss of TiO_2 nano-particles from the membrane was observed after a continuous 7-day RO trial [184, 185].

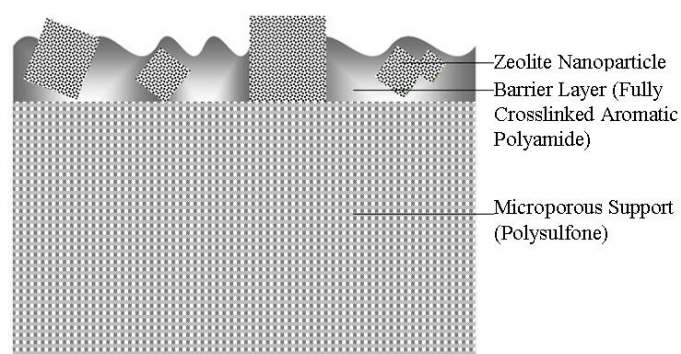
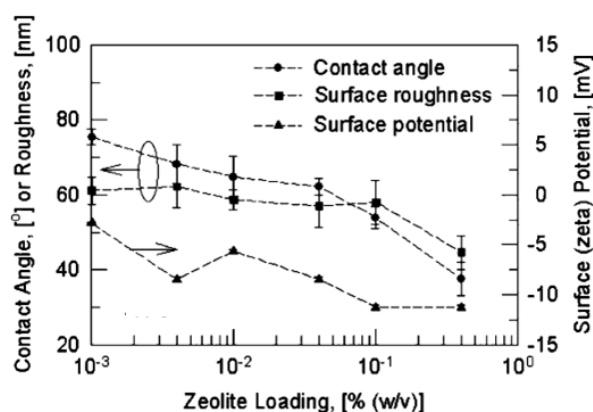
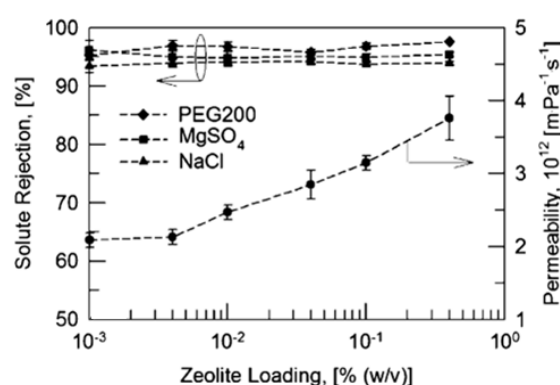


Figure 10. Schematic cross-section of zeolite nanocomposite membrane (Reprinted with permission from Jeong *et al.*, 2007) [186];

Zeolite nano-particles have also been used to prepare MMMs (Figure 10). First zeolite nano-particles are synthesized via a templated hydrothermal reaction. This is followed by a series of complex processes involving template removal, carbonization, sodium exchange and calcination [186]. The resultant NaA-type zeolite particles are in the size range of 50 – 150 nm with a Si / Al ratio of 1.5. These particles are reported to be very hydrophilic (contact angle $< 5^\circ$), with negatively charged 0.4 nm pores which are highly repulsive to anions. The zeolite nano-particles are dissolved into a cross-linking agent solution (trimesoyl chloride dissolved in hexane) before the interfacial polycondensation reaction takes place. This is different to dipping the previously formed membrane into a nano-particle-containing solution, as with the TiO_2 nanocomposite membrane. A homogeneous dispersion of zeolite particles is achieved using ultrasonication before the standard interfacial polymerization is carried out. RO membranes with various zeolite loadings were prepared and consequent changes in membrane characteristics were observed, *i.e.* the membranes were smoother, more hydrophilic and more negatively charged with increasing nano-particle loading. The MMM membrane exhibited 90 % of flux and a slight improvement in salt rejection relative to the hand cast TFC membrane without zeolite nano-particles. The authors suggest that this could be a result of enhanced Donnan exclusion by the zeolite particles and changes of membrane morphology [186, 187]. Figure 11 illustrates the changed surface properties and membrane separation performance as a result of variation in zeolite nano-particle loading.



(a)



(b)

Figure 11. Effect of zeolite loading dosage on

(a) surface properties, and

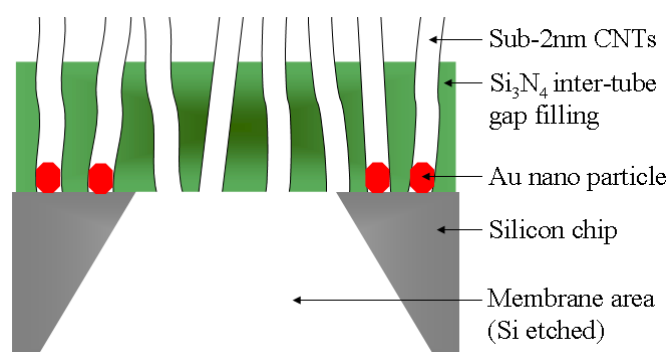
(b) separation performance

(Reprinted with permission from Jeong *et al.*, 2007) [186]

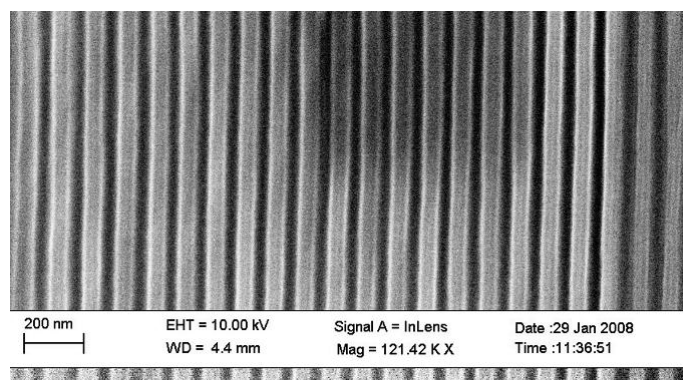
3.3.2 Carbon Nano-tube / Polymeric Membranes

Carbon nano-tubes (CNTs) have caught the attention of many researchers due to the similarity between their fluid transport properties and those of water transport channels in biological membranes [188]. Experimental results of fluid flow in a CNT membrane was first reported in 2004 [189]. Well aligned multi-wall CNTs were grown by catalytic chemical vapour deposition (cCVD) on the surface of quartz substrates. These were spin coated with polystyrene to seal the inter-tube gaps and plasma etching was used to open the tips of the CNTs. Shortly after this, experimental analysis of water transport in a solid polystyrene film membrane incorporating 7 nm diameter multi-wall CNTs was published. The observed flow

velocity is four to five orders of magnitude higher than the value expected from the Haagen-Poiseuille equation, which governs macroscale hydrodynamics [190]. Another fluid flow experiment with a CNT membrane synthesized using nanofabrication techniques has been reported (Figure 12(a)). This membrane contained double wall CNTs with $< 2\text{nm}$ diameter, and showed flow velocities of three to four orders of magnitude higher than the theoretical calculation [191]. Recently, water transport through template-grown carbon nanopipes (CNPs) of about 44 nm in diameter was investigated. These CNPs were synthesized using non-catalytic CVD, yielding an amorphous (or turbostratic) graphitic structure (Figure 12(b)). The presence of the template eliminates structural imperfections such as tortuosity, pore misalignment, and branching. The factor of flow enhancement over the predicted value is about 20, much smaller than in previous cases [192]. The authors suggest that this might be due to the different surface chemistry and structure compared to the CNTs in the previously cited articles, prepared by cCVD.



(a)



(b)

Figure 12. (a) Schematic of CNT membrane reported in [191];
(b) SEM micrograph showing cross-section of CNP membrane [192].

The fast water transport observed has led to many ongoing scientific discussions [188, 193, 194]. The origin of this extremely fast water transport in CNTs is not completely clear, and seemingly contradictory explanations have been reported by simulation studies on this topic [195-197]. It has been suggested that the development of a strong hydrogen-bonding network between the water molecules and the atomically smooth hydrophobic inner nanotube wall causes spontaneous imbibition. This subsequently leads to the formation of a vapour layer between the surface and the bulk flow, that facilitates the water transport in a slug flow manner [198-199]. On the other hand, it also has been argued that the frictionless water flow is due to the formation of a layer of liquid water molecules on the CNT walls, which provides 'shielding' of the bulk water molecules such that they flow faster [200].

Ion transport through the CNT channels has been investigated both experimentally and computationally. Transport of ions of various valences has been studied in double walled CNTs of 1 – 2 nm diameter, functionalized with negatively charged groups. Although the ion rejection is not sufficiently high for desalination, this study suggests that the ion exclusion mechanism in CNTs is dominated by electrostatic interactions (Donnan exclusion) rather than steric effects. This conclusion is based on the observation that solution pH and electrostatic screening length significantly influence ion rejection [191, 201]. Majumder's group have also demonstrated two methods to alter the selectivity of different ion species, namely alteration of pore size by CNT tip-functionalization, and voltage based gate control [202, 203]. Although monovalent salt rejection is not tested in either case, these studies have demonstrated the potential of altering pore properties to enhance selectivity.

A molecular dynamic simulation of RO using CNTs has been performed depending solely on physical size exclusion mechanisms. This shows that 0.8 nm CNTs can completely reject the salt whilst giving at least a 4 fold flux improvement over current state of the art TFC RO membranes, depending on the assumed packing density of the CNTs [204, 205]. Effects of charged functionalities, which are often present at both ends of CNTs, were not considered in this simulation. The effect of their presence would probably be to expand the CNT size regime as the formation of charged double layer can improve the salt rejection [193].

Mauter and Elimelech summarize previous research efforts into the development of CNT membranes for desalination, and forecast the necessary work on the next generation of CNT membranes [161]. The study concludes that whilst CNT membranes are promising for flux enhancement, more work is needed in the development of efficient synthesis methods to align arrays of single-walled CNTs, with sub-nanometre diameters, and also the development of tip-functionalization for more efficient salt rejection.

The fabrication of the CNT / polymeric membrane in the experimental studies described above [189-191], and in many other gas separation studies, involves multiple complex steps, such as catalytic growth of CNTs onto expensive substrates, polymer filling of the inter-tube spaces, substrate removal, and CNT tip opening via etching. Furthermore, the size distribution of the CNT diameters is still not small enough to complement the simulation studies performed. To overcome this problem, a patent has disclosed the blending of CNTs into solutions, preferably cross-linking agent solutions (trimesoyl of isophthalic chlorides), for formulation of composite polymeric membranes (Figure 13). In this way CNTs can be effectively embedded onto the barrier layer formed by conventional interfacial polymerization on a micro-porous polyethersulfone support [206]. The CNTs need to be functionalized to obtain better solubility in organic solvents, and in this patent the CNTs are functionalized with octadecylamine. The resulting membrane can be easily adapted into current filtration and RO systems, with the CNTs used being 0.8 nm in diameter. The water permeates through the membrane via both the conventional polymeric barrier layer and the embedded CNT pathways. A test is disclosed in the patent which compares membranes fabricated with and without embedded CNTs, to demonstrate the enhanced flow generated by the CNT pathways. With CNTs present a slightly higher salt rejection was achieved (97.69 % as compared with 96.19 %) and a near doubling of water flux ($44 \text{ L m}^{-2} \text{ day}^{-1} \text{ bar}^{-1}$ as compared with $26 \text{ L m}^{-2} \text{ day}^{-1} \text{ bar}^{-1}$) was obtained. However as the membrane disc that was synthesized was only 47 mm in diameter, studies on much larger surface area membranes are needed before large scale manufacturing methods can be developed.

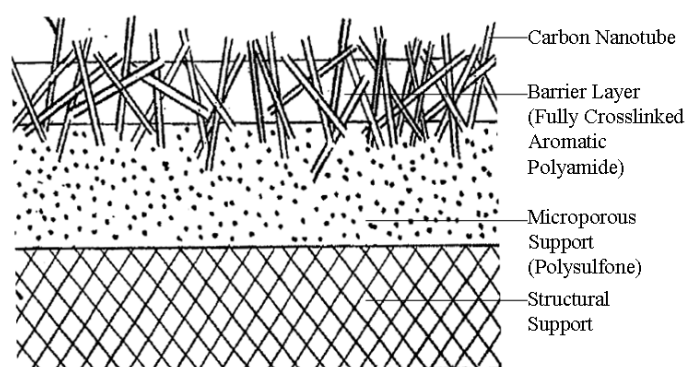


Figure 13. Schematic cross-section of CNTs embedded TFC membrane (Adapted from Ratto *et al.*, 2010) [206].

3.4 Biomimetic RO Membranes

The excellent water transport properties of biological membranes has led to the study of membranes incorporating aquaporins, which are proteins functioning as water-selective channels in biological cell membranes [207]. Membranes incorporating bacterial Aquaporin Z proteins have been reported to show superior water transport efficiency relative to conventional RO membranes [208]. Aquaporins were incorporated into the walls of self-assembled polymer vesicles constituted of tri-block co-polymer, poly(2-methyl-2-oxazoline)-block-poly(dimethylsiloxane)-block-poly(2-methyl-2-oxazoline). An initial permeability test was carried out on the aquaporin-triblock polymer vesicles by stopped-flow light-scattering experiments. The results reported give at least an order of magnitude improvement in permeability compared to commercially available TFC RO membranes [208]. Although a salt separation test has yet to be reported, extremely high salt rejection is expected from aquaporins since their functional biological performance is to only allow the passage of water molecules. Hence, they represent an ideal opportunity for the production of ultra pure water [208-210]. These studies have so far been limited to investigating water permeability properties across a barrier layer composed of aquaporins and triblock polymers. Many practical issues, such as identification of appropriate support materials, understanding of the resistance to membrane fouling, and even identification of an appropriate range of operating conditions must be carried out to develop this membrane for practical use.

The use of an NF membrane as a biomimetic membrane support has been reported [211]. A continuous phospholipid bilayer was successfully formed on a NTR-7450 membrane and fully covered it, using the vesicle fusion approach. Further study is needed to incorporate aquaporins into the phospholipid bilayer for practical use in water purification. A Danish Company named Aquaporin was founded in 2005 in order to develop these membranes for practical industrial use. The company has recently been awarded a patent on the method of fabricating membranes incorporating aquaporins (Figure 14) [212]. Rather than using triblock polymers the aquaporins are reconstituted into lipid bilayers fabricated using the Langmuir-Blodgett method, a vesicle fusion method, or they are spin-coated. The patent also discloses the two different orientations of the membrane: (i) a lipid bilayer incorporating the aquaporins is sandwiched between two hydrophilic porous support layers such as mica, polysulfone or cellulose; or (ii) a lipid bilayer incorporating aquaporins is assembled over a hydrophobic porous support membrane such as a porous PTFE film. In either case the patent

does not disclose any numerical data regarding the flux and salt rejection performance of the membranes, whereas severe fouling and concentration polarization are reported.

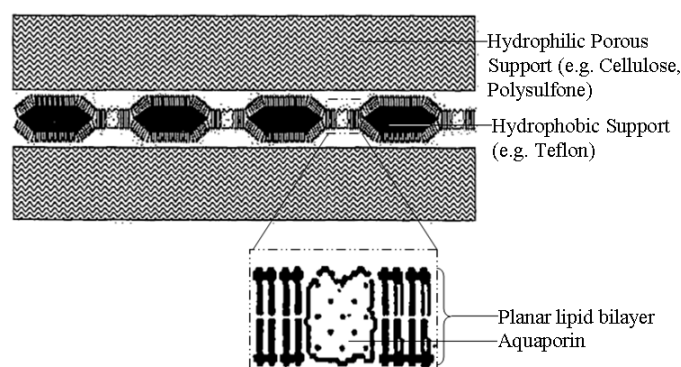


Figure 14. Schematic cross-section of Aquaporin embedded membrane (Adapted from Jensen *et al.*, 2010) [212].

4. Conclusions and Future Developments

RO desalination has more than half a century of industrial operation. Coupling this with the ability to handle a wide range of water sources makes it a strong candidate to tackle current and future water shortage problems. It is so far the most efficient technology for wastewater reclamation (tertiary treatment), and is one of the best performing technologies for desalting brackish water and sea water. The former is obviously a highly desirable solution in densely populated regions since it solves two problems simultaneously, namely wastewater treatment and enhancement of fresh water supply. Alongside the advancements in other aspects of RO technology, the development of membrane materials has undeniably made RO desalination more economic by increasing performance and efficiency. Nevertheless, the search for multifunctional membrane materials that offer higher permeability, high ion and organic contaminant rejection, and operational robustness is still ongoing. This research is expected to benefit the desalination industry by lowering the energy cost and membrane area required; simplifying pre-treatment processes; providing lower membrane maintenance costs; potentially achieving single pass RO desalination; and increasing plant capacity. In summary it promises to make significant reductions in both capital investment and operating costs.

The development of polymeric membrane materials has gone through three main stages: (i) empirical trial-and-error testing of polymers; (ii) selecting suitable polymerisation reactants

based on better understanding of polymer chemistry; and (iii) closely monitoring membrane morphology with the aid of advanced characterization tools. Despite major earlier breakthroughs such as the Loeb-Sourirajan asymmetric membrane (1960s), fully crosslinked aromatic TFC membrane (1970s to 1980s), and controlling morphological changes by monitoring polymerisation reactions (1990s), the evolutionary improvement of a commercial RO membrane has been rather slow during the first decade of this century. Another key limitation of commercial RO membranes is degradation by chlorine, which requires de-chlorination of the RO feed and re-chlorination of the RO permeate. Furthermore, excessive pressure is required to overcome the resistance arising when membranes become fouled. The evolutionary improvement of membranes solely prepared from polymeric materials seems to be approaching saturation.

Various nano-structured RO membranes have been proposed to offer attractive permeability characteristics, and many scientists believe that nanotechnology could possibly bring revolutionary advancements to the desalination industry. However, the development of such membranes is only in the initial stages and many problems are yet to be overcome. The two major practical challenges are the high cost of nano-structured materials, and the difficulty in scaling up nano-membrane manufacturing processes for commercial use. In addition, health and safety issues around the use of nano-materials have to be addressed in the domestic water industry, particularly with respect to the use of nano-particles. Currently, nano-structured RO membranes appear to be in the same position as the initial development phase of polymer RO membranes, albeit with the latter now being a successful competitor in the market. The novel membrane materials are expected to outperform current RO membranes especially those listed in Table 1, however strong competition is foreseen, particularly via the introduction of 16 and 18 inch RO membrane elements. In addition, more resistance to biological and chemical attack is also very desirable.

Polymeric membrane fabricated via rigid star-shaped amphiphilic molecules has been a break-through since interfacially polymerised RO/NF membrane has been dominating for more than 30 years. Though it offers the possible engineering of membrane structure in the nano-scale, there is no report of an RO membrane fabricated by this means so far.

Although the proven permeability improvement of zeolite thin film nano-composite membranes is the lowest when compared with membranes incorporating CNTs and aquaporins, they appear to be more readily adaptable to commercial use due to their similarity to current commercial RO membranes. Nonetheless, their cost effectiveness needs to be investigated because significant additional cost is expected to arise from the complex

synthesis of nano-particles, and the extra energy required to effectively disperse the nano-particles onto the barrier layer. Further technical studies such as optimisation of nano-particle size and dosage, elimination of crystalline defects, and simplification of nano-particle synthesis procedures are also needed.

As with zeolite nano-composite membranes, the incorporation of CNTs into membranes, disclosed in the patent granted to NanOasis, shows a promising and scalable production technique that is almost identical to conventional RO membrane production [206]. However the manufacturing cost of the suggested 0.8 nm single walled CNTs for RO membranes can range from US\$1,800 per gram and upwards [213]. The cost of CNT tip fictionalization and the energy required to homogeneously disperse the CNTs also have to be added. Unless combined savings from the enhanced permeability and superior membrane properties are proven, the incorporation of CNTs into membranes for water production appears economically unfavourable. However, the potential performance can be further improved by more dense and ordered packing of the CNTs. Instead of incorporation of CNTs into polymer solutions, *in-situ* growth of CNTs via ceramic templating could offer a better method of engineering these novel membranes.

Theoretically, biomimetic membranes offer the highest permeability, but this conclusion is solely derived from transport velocity measurements of water molecules through individual aquaporin channels rather than conventional membrane permeability tests. In addition, the packing density of aquaporins in a membrane can significantly affect the overall permeability performance. Identification of a suitable membrane support is another technical problem preventing practical implementation. Despite the almost absolute salt rejection, these biomaterials are relatively unstable, with particularly severe fouling having been observed. The durability of the membrane is therefore expected to be relatively low. Most importantly, the fabrication process for these membranes are amongst the most complex of all the systems analyzed in this review, and are also possibly the most expensive.

While nanotechnology is leading the way in the development of novel RO membranes for desalination, there are many fundamental scientific and technical aspects that have to be addressed before the potential benefits may be realized. An example target is the development of single-pass RO using multifunctional membranes, eliminating the need for pre-treatment. At this stage these novel technologies are still too expensive for practical application, and hence the development of novel RO membranes with improved salt rejection and permeability at a reasonable cost is still the key focus of RO desalination technology.

Acknowledgement

The authors would like to acknowledge the University of Bath for supporting this work via the award of an Overseas Research Student Excellence Scholarship to Kah Peng Lee, EPSRC (grant EP/G045798/1), and EU (grant PIRG03-GA-2008-230876) for funding support. The contents reflect only the authors' views and not the views of the European Commission.

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